NOLTR 66-32

POLISHES AND ETCHES FOR TIN TELLURIDE, LEAD SULFIDE, LEAD SELENIDE, AND LEAD TELLURIDE: SUPPLEMENT

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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Prepared by:
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ABSTRACT: This report is a continuation of NOLTR 63-156[1]. Together, the two reports present a review of chemical and electrolytic polishes and dislocation etches for SnTe, PbS, PbSe, and PbTe, covering the period from 1907 through 1965. The present report also describes a new polish and a new dislocation etch for tin telluride, as well as tests on and improvements in some of the polishes reported in earlier publications.

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Polishes and Etches for Tin Telluride, Lead Sulfide, Lead Selenide, and Lead Telluride: Supplement

This is the concluding report of a study of chemical and electrolytic polishes and dislocation etches for SnTe, PbS, PbSe, and PbTe, carried out at the U. S. Naval Ordnance Laboratory, White Oak, during the period, June 1963 through February 1966. It presents the results of work done under Foundational Research Task Fr-46 and is for information only.

The author is indebted to Dr. Bland Houston for supplying the various crystals and for helpful advice, to John V. Gilfrich for taking the Laue photographs and diffractometer measurements, and to Harvey Yakowitz for taking the Kossel photograph.

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Captain, USN
Commander

W. W. Scanlon

W. W. SCANLON
By direction

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Chapter 1

INTRODUCTION

This report describes chemical polishes for SnTe, PbS, and PbTe, and a dislocation etch for SnTe.

The polishes are for removing damaged surface layers formed by grinding or mechanical polishing, for removing pits caused by etching, and for producing smooth, shiny surfaces. Damage-free surfaces such as these are necessary for dislocation density determinations by the etch pit method, optical reflectivity measurements, single crystal X-ray studies, and for high precision density determinations.

Dislocation etches produce pits where dislocations intersect the surface of the crystal. These pits are observed along grain boundaries, traces of active slip planes, at points randomly distributed over the surface, and in regions where the crystal has been damaged. The density of the pits, the average grain size, etc., give an estimate of the quality of the crystal.

Descriptions of the polishes and of the etch are given in Chapters II and III, respectively. Paragraphs labelled "Test Results" give the results of tests made by the author on some previously published polishes.

Chapter II

POLISHES

A. Tin Telluride

FAUST AND SAGAR[2,1] The original procedure had the disadvantage of frequently leaving a whitish haze (and sometimes dark stains) on the samples when they were polished for a long enough time (3-5 minutes) to remove the scratches formed by previous mechanical polishing[1]. An additional step to the procedure improved the surfaces somewhat[1].

The following procedure further reduced the amount and frequency of whitish haze and stains on the polished sample surfaces. The recipe for the polishing solution is the same as that previously described[2,1], namely, 6 parts by vol. glacial acetic acid + 3 parts 70% HNO_3 + 1 part 49% HF. The sample is cleaned with benzene and dried on lens paper. It is then immersed in the polishing solution, at 25°C, and stirred with gentle swirling. When the sample is sufficiently polished, the solution is diluted with twice its volume of glacial acetic acid, with stirring. Using Teflon-coated tweezers, it is removed from the solution, rinsed with a stream of methanol, and immersed in methanol in a polyethylene container. The container is swirled 1-2 minutes to thoroughly wash the sample. The sample is then removed, rinsed in fresh methanol, and dried on lens paper.

NORR. The sample is mounted in a stainless steel jig assembly and ground flat on No. 600 grit SiC paper. It is then transferred to a polycarbonate jig assembly (to which it is attached with paraffin) and polished with Carborundum No. 50 grit Al_2O_3 optical finishing powder on a paraffin lap. Finally, it is polished with Linde A abrasive on a paraffin lap. A 1:1 solution of Joy detergent in ethanol is used as a lubricant with each of the abrasives. The sample, jig assembly, and hands should be thoroughly cleaned after each step of grinding and polishing.

The solution for chemical polishing is prepared by dissolving 0.35 g I_2 in 40 ml ethanol (or methanol) and then adding 10 ml dist. H_2O and 4.0 ml 49% HF. A polyethylene beaker is used to avoid contamination from the container.

A piece of twill jean cloth* is stretched over a smooth Teflon plate and saturated with the solution, at 25°C. It is

*K. S. 2423 twill jean cloth, Exeter Mfg. Co., Inc., Exeter, N. H.

recommended that the hands be protected from the solution with polyethylene gloves. The sample (still mounted in the polycarbonate jig assembly) is polished by lightly rubbing it over the wet twill jean cloth, using a figure eight motion, for 15-20 minutes. Periodically, additional solution must be added to keep the cloth saturated. The sample is then rinsed in a stream of methanol, followed by a stream of distilled water, and dried on lens paper. After demounting, it is soaked 2-3 times in fresh benzene to remove any adhering paraffin and dried on lens paper.

The SnTe crystals polished by the author were grown by the Czochralski or "pulling" method.

The polish produced clean, mirror-like surfaces somewhat flatter than those obtained with Faust and Sagar's polish. The surfaces have been used successfully for reflectivity measurements[3]. Back-reflection Laue photographs, diffractometer measurements, and a Kossel photograph indicated the surfaces were free of major strains. However, when two of the samples were etched with the SnTe etch described later in this report, pitted scratches were formed on the surface. This indicates that although these polished surfaces were free of major strains (as shown by the X-ray data), remnants of scratch damage still remained.

B. Lead Sulfide

BREBRICK AND SCANLON[4] Although the author of this report did not find this polish satisfactory[1], it was used, apparently successfully, by Geick[5] to obtain surfaces which were used for reflectivity measurements in the 40 μ to 2 mm wavelength region.

URUSOVSKAYA, ET AL.[6] The polishing solution consists of 3 parts of HNO_3 and 2 parts of HCl. Polishing is carried out at 55-60°C, with stirring. A layer 8 μ thick is removed in 1 minute. The lead sulfide samples used in these experiments were reported to be quite impure.

Test Results. Two samples were tested--one a piece of n-type PbS from a natural source, and the other a p-type crystal grown by the Bridgman-Stockbarger method. The surfaces were cleavage surfaces ground on No. 600 grit SiC paper lubricated with a 1:1 solution of Joy detergent in ethanol.

The polishing solution consisted of 15 ml 70% HNO_3 + 10 ml 37% HCl. The samples were immersed in the solution, at 55-60°C, with stirring, for 5 minutes, rinsed in a jet of distilled water to remove the layer of gray material on the surface, and

dried on lens paper. The n-type sample had some thin brown stains on one side and the p-type sample had some spots of gray film. Both had an etched or roughened appearance at 300X.

In an attempt to get better surfaces, the samples were ground and polished as before. Following rinsing in a jet of distilled water, the wet crystals were immersed in 10% acetic acid for 2 minutes, rinsed with distilled water, and dried on lens paper. The results were the same. No polishing action was observed.

The success of this polish on the samples of Urusovskaya, et al., and its failure on the author's may be due to the impurities in the formers' samples.

C. Lead Telluride

SCHMIDT.[7] The present author found that samples polished by this method were mostly covered with a blue-black film[1]. The following modified procedure gave a clean, mirror-like surface.

The samples are ground flat on No. 600 grit SiC paper lubricated with an aqueous soap solution, and then ground on dry No. 4/0 grit emery paper. After each step, both the sample and the hands are thoroughly cleaned and dried.

The polishing solution is prepared by dissolving 5 g tartaric acid in 50 ml 30% H_2O_2 and then adding 50 ml glacial acetic acid. Polising is carried out in two steps. Step A: Using a figure eight motion, the samples are polished 2-3 minutes on a piece of twill jean cloth (on a flat glass plate) sprinkled with Linde A abrasive and saturated with the polishing solution, at 25°C. They are then rinsed with distilled water, cleaned with lens paper soaked in acetone, again rinsed with distilled water, and dried on lens paper. Step B: The samples are polished for 2-3 minutes on a second piece of twill jean cloth (on a flat glass plate) saturated with the polishing solution, but without the Linde A abrasive. Immediately thereafter, they are rinsed, first with distilled water, and then with acetone.

The method has the disadvantage of occasionally forming scratches during polishing. (See Fig. 1 (50 min.)). These scratches may be caused by minute particles which broke off of the edges of the sample as it was polished.

This procedure was successful on all the PbTe samples tested, except for two Na-doped crystals. One contained 0.06 and the other 0.02 at. % Na. Both tended to develop a hazy

surface appearance, particularly the first one. Better results were obtained on these samples by reducing the amount of tartaric acid in the polishing solution from 5 g to 1-2 g.

Surface Quality. A sample from a p-type, "pulled" crystal was ground on dry No. 4/0 grit emery paper, parallel to one of its cleavage planes, and polished using Steps A and B described above. After polishing, it was etched with a modified Coates[8] etch*. The etch brought out residual scratches as well as grain boundaries, traces of active slip planes, etc. These residual scratches are regions of disturbed material formed during mechanical grinding. When Steps A and B were only 5 minutes each, the surface, when etched, showed very many residual scratches. (See Fig. 1.) Using a 5 minute Step A, a total of about 50 minutes of Step B was required to remove the residual scratches. These results are typical of the results obtained by the author on several samples.

LORENZ.[9] The polishing solution is composed of satd aq $K_2Cr_2O_7$ and conc. HNO_3 mixed in a volume ratio of 4.2-5.0, ($K_2Cr_2O_7$: HNO_3) 4.5 being the optimum ratio. The samples to be polished are placed in a rotating pyrex basket immersed in the solution, at 25°C. Satisfactory polishing can also be obtained, according to the report, by placing the samples directly in the solution and vigorously stirring with a magnetic stirrer. The rate of surface removal varies between 20 and 40 μ/min. When the samples appear to be adequately polished, they are removed and rinsed in water and dried. Sometimes a polished sample may have a barely visible golden film. This can be removed by placing it in 50% NaOH, heating the solution to 100-120°, and then allowing the solution to cool down to room temperature. The sample is then rinsed in dilute HCl, thoroughly rinsed in distilled water, and finally dried.

Test Results. Insufficient tests have been made by the author to properly evaluate Lorenz's polish.

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*The freshly polished sample was immersed in a solution containing 10 ml aq KOH (satd at 20°C) + 10 ml glycerol + 1.0 ml 30% H_2O_2, for 5 min, at 25°C, with light stirring. It was then rinsed with distilled water and dried on lens paper.

Chapter III

DISLOCATION ETCHES

A. Tin Telluride

NORR. The etching solution is prepared by adding 10 ml methanol to 45 ml 33% aq KOH, cooling to 25°C, adding 10 ml 30% H_2O_2, and again cooling to 25°C. The sample to be etched is first polished on one of its {100} surfaces by the method of Norr (see Sect. II-A-NORR), rinsed with methanol, and immersed in the etching solution while the sample surface is still wet with methanol. Every 5-10 sec the sample is lightly tapped to loosen the gas bubbles that form on the surface. (Actual stirring is avoided because it greatly increases the number of gas bubbles.) At the end of 5 min it is rinsed with methanol followed by distilled water and dried on lens paper.

On one of the samples etched by the above method, sharp, pitted grain boundaries, pitted scratches, and some randomly distributed pits were formed. Some of the pits were circular and some were oval. The background between them was rough. The second sample (from a different crystal), similarly etched, gave like results except that there were some small unattacked areas and some areas with a whitish film and some stains. Repeated polishing and etching of these two samples consistently gave the same results. Several other samples, etched in the same manner, however, failed to give good etch pit patterns.

From these results, it does not appear that this is a good general dislocation etch for SnTe--the etch seems to be successful on some samples, but not on others.

Chapter IV

SUMMARY

Descriptions of chemical polishes and of a dislocation etch, together with tests made on some of them by the author, have been given for SnTe, PbS, and PbTe.

There is still a need for a polish for PbS and a good dislocation etch for SnTe. Also, an improved polish for PbSe and a room temperature dislocation etch for PbS would be helpful.

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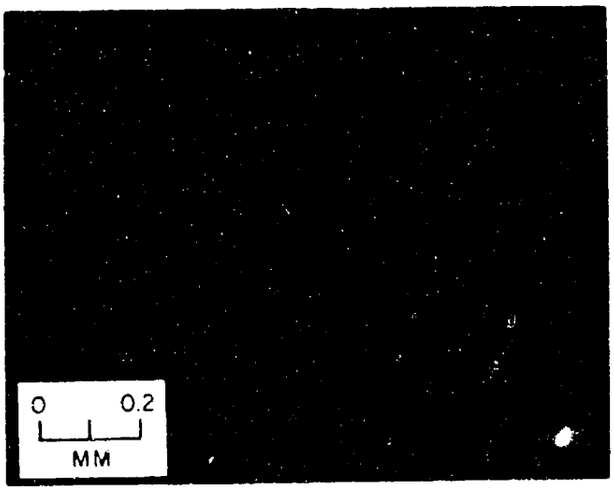

STEP B = 3 MIN

STEP B = 13 MIN

STEP B = 28 MIN

STEP B = 58 MIN

FIG. 1 GRADUAL REMOVAL OF RESIDUAL SCRATCHES FROM Pb Te BY SCHMIDT'S POLISH (MODIFIED)

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